

Scalar Static Polarizabilities of Lanthanides and Actinides.

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We calculate scalar static polarizabilities for lanthanides and actinides, the atoms with open $4f$ or $5f$ subshell. We show that polarizabilities of the low states are approximately the same for all states of given configuration and present a way of calculating them reducing valence space to just two or three valence electrons occupying $6s$ and $5d$ states for lanthanides or $7s$ and $6d$ states for actinides while $4f$ and $5f$ states are considered to be in the core. Configuration interaction technique is used to calculate polarizabilities of lanthanides and actinides for all states of the $4f^n 6s^2$ and $4f^{n-1} 6s^2 5d$ configurations of lanthanides and all states of the $5f^n 7s^2$ and $5f^{n-1} 7s^2 6d$ configurations of actinides. Polarizability of the electron core (including f -orbitals) has been calculated in the RPA approximation.

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I. INTRODUCTION

The main characteristic of a neutral atom which determines its interaction with the environment is its polarizability. The van der Waals forces between atoms, atom-wall interaction, interaction of neutral atoms with laser electric field in an optical lattice are all related to polarizabilities (see, e.g. [1, 2]). Interest to accurate measurement and calculations of atomic polarizabilities rose over the last decade with the development of next generation of atomic clocks based on optical transitions [3, 4]. Accuracy of optical clocks is mostly limited by the blackbody radiation shift (BBR) (see, e.g. [5–8]) which is proportional to differential polarizability of two atomic clock states. There is a review by Mitroy *et al* [9] which describes in detail current status of the experimental and theoretical study of atomic polarizabilities. In brief, it is as follows. Polarizabilities are well studied for ground states of noble gases and for ground and some excited states of atoms with simple electron structure, i.e. atoms which have one, two or three valence electrons above closed shells. Experimental data for excited states is poor. This is one of the motivations for accurate atomic calculations. Having accurate values of atomic polarizabilities for excited states is important for estimation of the BBR shift and for finding the so called *magic* frequencies of laser field that makes optical lattice for which the electric dynamic energy shift of both clock states are the same so that clock frequency is not affected by lattice field.

In contrast to relatively rich data for atoms with simple electron structure, the situation for atoms with open d or f shells is very much different. Apart from very few exceptions, the experimental data is practically absent. Theoretical data is presented by a single unpublished work by Doolen [10] which, in spite of being unpublished, is widely cited in textbooks and databases (see, e.g. [11, 12]). It uses a relativistic linear response method [13], estimated uncertainty is 25%.

Knowing polarizabilities of open-shell atoms is important for many applications. For example, it was sug-

gested in Ref. [14] to search for positron-atom bound states through resonant annihilation. The method would work for atoms with open shells which have low-lying excited states within the ground state configuration [15, 16]. Kinetic energy of scattering positron is spent on exciting the atom and positron is bound to the exciting state. Polarizability is an important characteristic of the atoms governing their ability to bind a positron. In this paper we argue that polarizabilities of all states of the same configuration are approximately the same. Therefore, if positron is bound to the ground state it is very likely to be bound to an excited state of the same configuration.

Lanthanides and actinides are also used in many other important studies. For example, Yb and Er are considered for very precise atomic clocks [4, 17]; parity non-conservation has been measured in Dy [18] and Yb [19]; Dy and Er are used to study quantum gases [20, 21]; Th is considered for ultra-precise nuclear clock [22], etc. The heaviest of the actinides approach an important area of superheavy elements [23]. In terms of electron structure, there is practically no experimental data for superheavy elements, all data comes from theory and polarizability is one of the most important characteristics.

In this paper we try to address the lack of data on polarizabilities of lanthanide and actinides. We propose a method of calculation which reduces the calculation of polarizabilities of lanthanides and actinides to calculations for a system with two or three valence electrons. The approach is based on the assumption that residual Coulomb interaction between f and other valence electrons is small so that total angular momenta of each subsystem are still good quantum numbers. This allows us to attribute f -electrons to the core reducing the problem to calculation of the polarizabilities of the $6s^2$ or $6s^2 5d$ configurations of the valence electrons for lanthanides and $7s^2$ or $7s^2 6d$ configurations for actinides. To check the approach we have performed test calculations for few systems in which f -electrons were treated as valence states. The agreement between two approaches is very good. There is also surprisingly good agreements with early calculations by Doolen [11]. As a rule, the difference be-

tween our results and those of Doolen [11] is much less than the 25% uncertainty claimed in [11]. There is also good agreement with the experimental data for uranium. However, we have significant disagreement with the results of the measurements of the dynamic polarizabilities for Dy [24] and Er [25]. The possible reasons for this disagreement are discussed.

II. GENERAL FORMALISM

Second-order Stark shift of atomic energy level in static electric field \mathcal{E} can be written as

$$\Delta E_a = -\frac{1}{2}\alpha(a)\mathcal{E}^2, \quad (1)$$

where polarizability α is the sum of scalar and tensor terms

$$\alpha(a) = \alpha_0(a) + \frac{3M_a^2 - J_a(J_a + 1)}{J_a(2J_a - 1)}\alpha_2(a). \quad (2)$$

Here J_a is the total angular momentum of the atom and M_a is its projection on the direction of the electric field. Scalar polarizability $\alpha_0(a)$ and tensor polarizability $\alpha_2(a)$ can be expressed via sums over complete sets of intermediate states involving matrix elements of the electric dipole operator \mathbf{D} (in length form $\mathbf{D} = -e \sum_i \mathbf{r}_i$)

$$\alpha_0(a) = \frac{2}{3(2J_a + 1)} \sum_n \frac{\langle a || \mathbf{D} || n \rangle^2}{E_a - E_n}, \quad (3)$$

$$\alpha_2(a) = 2 \sqrt{\frac{10J_a(2J_a - 1)}{3(2J_a + 3)(2J_a + 1)(J_a + 1)}} \times \sum_n (-1)^{J_a + J_n} \left\{ \begin{matrix} 1 & 1 & 2 \\ J_a & J_a & J_n \end{matrix} \right\} \frac{\langle a || \mathbf{D} || n \rangle^2}{E_a - E_n}. \quad (4)$$

Here $|a\rangle$ and $|n\rangle$ are many-electron atomic states and E_a and E_n are corresponding energies. Tensor polarizability (4) is none-zero for $J_a \geq 1$ while scalar polarizability is none-zero even for $J_a = 0$.

In this paper we consider only scalar polarizabilities.

A. Polarizabilities of closed-shell atoms

For closed-shell atoms tensor polarizability is zero and scalar polarizability is given by

$$\alpha_0 = \frac{2}{3} \sum_n \frac{\langle a || \mathbf{D} || n \rangle^2}{E_0 - E_n}. \quad (5)$$

In the random-phase approximation (RPA) expression (5) is reduced to the sum over single-electron matrix elements

$$\alpha_0 = \frac{2}{3} \sum_{cn} \frac{\langle c || \mathbf{d} + \delta \mathbf{V} || n \rangle \langle n || \mathbf{d} || c \rangle}{\epsilon_n - \epsilon_c}, \quad (6)$$

TABLE I: Comparison of calculations of scalar polarizabilities of some noble gases with experimental values presented in [9]. Values are in atomic units.

element	calculation	experiment
Ar	10.77	11.08
Kr	16.47	16.74
Xe	26.97	27.34

TABLE II: Contributions to scalar polarizabilities of some atoms with open f -shell from core states (below the $4f$ or $5f$ states), $4f$ ($5f$), and $6s$ ($7s$) states. Values are in atomic units.

element	core	$4f^{N-2}(5f^{N-2})$	$6s^2(7s^2)$	Total
Dy	-3.3	-1.9	215	209.8
Er	-3	-2.1	195.4	193.3
Yb	-2.6	-2.5	183.7	178.6
Pu	-2	-2	216.6	212.6

where $\mathbf{d} = -e\mathbf{r}$ is the single-electron electric dipole operator, $\delta \mathbf{V}$ is correction to the core potential due to core polarization by external electric field; summation goes over core states c and complete set of single-electron orbitals n . The energies ϵ_c and ϵ_n are the Hartree-Fock energies of single-electron orbitals n and c . Note that the core polarization correction $\delta \mathbf{V}$ is included in one of the electric dipole matrix elements only. This is because for a closed-shell system there is only one infinite chain of RPA diagrams standing between two electric dipole operators. It can be attributed to one of the operators but not to both [26].

The RPA approximation (6) gives good accuracy for noble gases (see Table I). It is also sufficiently accurate for the polarizabilities of closed-shell atomic cores. It is widely used in the calculations of atomic polarizabilities in which core and valence contributions are calculated separately and then added together.

Formally, Eq. (6) can be used for any closed-shell systems, such as e.g. Ba, Yb, etc. It can be even used for open-shell systems if fractional occupation numbers

formalism is used. However, the calculated RPA polarizability of such systems is usually overestimated. This is due to neglecting of important contribution of inter-electron correlations. Correlations produce additional attraction between electrons making the atom to be more compact and reducing its polarizability. The RPA calculations can still be used for rough estimations and for the study of relative contributions of different atomic subshells. Table II, in which RPA polarizabilities of f-elements are presented, shows that the polarizabilities of f-elements are strongly dominated by external 6s- and 5d-electrons while the contribution of 4f-electrons is small. This means that the correlations should be treated accurately for two or three valence electrons while they can be neglected in other contribution. Inclusion of correlations is discussed in section III.

Note that the contribution of the f -states to the polarizability is negative (as well as the total contribution of the lower core states). It may look as an unexpected result since all terms in the exact expression (5) are positive. Total polarizability of the ground state is always positive. This is just a reflection of the well known fact that the second-order perturbation correction to the energy, which is related to polarizability via (2), is always negative. However, in the RPA approximation (6) only total polarizability is positive. Partial contributions might be negative due to the different sign of the $\langle c|\mathbf{d} + \delta\mathbf{V}|n\rangle$ and $\langle c|\mathbf{d}|n\rangle$ matrix elements. This only happens for lower states in the core and can be explained by screening of the external electric field in atoms [27]. The screened field has complex oscillating behavior inside atomic core often having different sign on wide range of distances. Note that screening is treated pretty accurately in the RPA approximation, e.g. Schiff theorem (complete screening of external electric field by electrons at the nucleus of an atom) fulfills exactly [27].

B. Polarizabilities of compound systems

To derive a way of calculating polarizabilities of complicated many-electron systems we start from a very general statement. If the system can be divided into two subsystems so that the total wave function is the product of wave functions of each subsystem connected by Clebsh-Gourdan coefficient then the polarizability of the whole system is the sum of polarizabilities of two subsystems. Such presentation is possible when residual Coulomb interaction between electrons of the two subsystems is small.

A case when the total angular momentum of one of the subsystems is zero is widely used in the calculations of the atomic polarizabilities. The total polarizability is presented as a sum of the contributions from closed-shell atomic core and from valence electrons. These contributions are calculated separately and then added together. Note that there are also cross contributions caused by Pauli principle. Calculation of polarizabilities of one

subsystem is affected by the other subsystem. States occupied by electrons of other system must be excluded from the summation over intermediate states due to Pauli principle. These contributions are usually small and we will ignore them in our consideration. There are also cancellations between Pauli-forbidden contributions to each of the polarizabilities.

We will consider a non-trivial case when total angular momentum of both subsystems is not zero. The wave function of the whole system is

$$|a\rangle = \sum_{M_1, M_2} C_{J_1 M_1 J_2 M_2}^{J_a M_a} |a' J_1 M_1\rangle |a'' J_2 M_2\rangle, \quad (7)$$

where J_a, M_a are the total angular momentum of the system and its projection, J_1, M_1 and J_2, M_2 are total angular momenta and projections for each subsystem, $C_{J_1 M_1 J_2 M_2}^{J_a M_a}$ is the Clebsh-Gourdan coefficient.

The electric dipole operator \mathbf{D} in the expression (3) for the scalar polarizability can be written as a sum $\mathbf{D} = \mathbf{D}_1 + \mathbf{D}_2$ in which summation in \mathbf{D}_1 goes over electrons of first subsystem and summation in \mathbf{D}_2 goes over electrons of second subsystem. Let us consider the contribution of \mathbf{D}_2 to the polarizability (3). States $|n\rangle$ which contribute to the polarizability can be written as

$$|n\rangle = \sum_{M_1, M_3} C_{J_1 M_1 J_3 M_3}^{J_n M_n} |n' J_1 M_1\rangle |n'' J_3 M_3\rangle. \quad (8)$$

Here first part of the wave function is the same as in (7) and second part satisfies selection rules for electric dipole transition between states $|a''\rangle$ and $|n''\rangle$, they have opposite parity and $J_3 = J_2, J_2 \pm 1$.

Substituting (7) and (8) into the square of the electric dipole matrix element we get

$$\begin{aligned} \langle a|\mathbf{D}|n\rangle^2 &= \begin{pmatrix} J_a & 1 & J_n \\ -M_a & 0 & M_n \end{pmatrix}^{-2} \times \\ &\left[\sum_{M_1, M_2, M_3} C_{J_1 M_1 J_2 M_2}^{J_a M_a} C_{J_1 M_1 J_3 M_3}^{J_n M_n} (-1)^{J_2 - M_2} \times \right. \\ &\left. \begin{pmatrix} J_2 & 1 & J_3 \\ -M_2 & 0 & M_3 \end{pmatrix} \right]^2 \langle a'' J_2|\mathbf{D}|n'' J_3\rangle^2 = \\ &(2J_a + 1)(2J_n + 1) \left\{ \begin{matrix} J_a & 1 & J_n \\ J_3 & J_1 & J_2 \end{matrix} \right\}^2 \langle a'' J_2|\mathbf{D}|n'' J_3\rangle^2. \end{aligned} \quad (9)$$

Here formula (12.1.6) from Ref. [29] was used. Noting that calculation of the polarizability involves summation over different values of total angular momentum J_n and using

$$\sum_{J_n} (2J_n + 1) \left\{ \begin{matrix} J_a & 1 & J_n \\ J_3 & J_1 & J_2 \end{matrix} \right\}^2 = \frac{1}{(2J_2 + 1)} \quad (10)$$

(see (12.2.15) from Ref. [29]), the expression (3) is reduced to

$$\alpha_0(a'') = \frac{2}{3(2J_2 + 1)} \sum_{n''} \frac{\langle a'' J_2|\mathbf{D}|n'' J_3\rangle^2}{E_{a''} - E_{n''}}. \quad (11)$$

We see that the contribution of \mathbf{D}_2 into total polarizability of the system is reduced to calculation of the polarizability of second subsystem as if there is no first subsystem. Expression (11) does not depend neither on the total angular momentum J_1 of first subsystem nor on the total angular momentum J_a of the whole system.

C. Application to f-elements

To calculate polarizabilities of f-elements using approach considered in previous section we divide all valence electrons into two subsystems, one has f-electrons only and other has all remaining electrons, namely two s-electrons or two s-electrons and one d-electron. We will consider lanthanides as an example. However, the same consideration is valid for actinides as well.

The wave function lowest states of lanthanides can be written as either

$$|a\rangle = \sum_{M_1, M_2} C_{J_1 M_1 J_2 M_2}^{J_a M_a} |4f^n J_1 M_1\rangle |6s^2 J_2 M_2\rangle, \quad (12)$$

or

$$|a\rangle = \sum_{M_1, M_2} C_{J_1 M_1 J_2 M_2}^{J_a M_a} |4f^{n-1} J_1 M_1\rangle |6s^2 5d J_2 M_2\rangle, \quad (13)$$

where J_a is the total angular momentum of the atom, M_a is its projection, J_1, M_1 are the total angular momentum and its projection of the $4f^n$ or $4f^{n-1}$ subsystem, J_2, M_2 are the total angular momentum and its projection for the $6s^2$ or $6s^2 5d$ subsystem, $C_{J_1 M_1 J_2 M_2}^{J_a M_a}$ is the Clebsch-Gordan coefficient. The quality of the approximation (12) or (13) for lanthanides can be illustrated by similarities in the spectra of neutral atoms and their double (or triple) ionized ions.

Applying the consideration of previous section we see that the calculation of polarizabilities of lanthanides is reduced to calculation of the polarizability of unfilled f-subshell and the polarizability of the remaining $6s^2$ or $6s^2 5d$ valence electrons.

As we have seen in section II A the contribution of f-electrons into polarizability is small. It can therefore be calculated in a single-configuration approximation with the use of fractional occupation numbers as discussed in section II A. It is the best to attribute the $4f$ electrons to the core so that their contribution to the self-consistent Hartree-Fock potential and to polarizability is calculated in a similar way with the use of fractional occupation numbers.

The dominant contribution to the polarizabilities comes from valence $6s$ and $5d$ electrons. Its calculation is now reduced to the calculation of the polarizability of two or three valence electrons system. The calculations for the $4f^n 6s^2$ configuration are reduced to the calculations for the $6s^2$ configuration as for ytterbium [37]; the $4f^{n-1} 6s^2 5d$ configuration is reduced to the $6s^2 5d$ one as in lutetium. No further approximation is needed

and full power of the configuration interaction technique combined with the many-body perturbation theory (the CI+MBPT method [30]) can be used. The details of the calculations for few valence electron systems can be found in our earlier works [30–32].

Note that since expression (11) does not depend on the total angular momentum of the atom, the scalar polarizability of the atom in this approximation is the same for all states of the same configuration. We have demonstrated this already for erbium in our previous work [17].

D. Application to d-elements

One may argue that the approach developed above should also work for atoms with open d -shells. Indeed, some of the supporting arguments do work for such atoms. For example, the contribution of the d -states into polarizabilities of atoms with open d -shells is small. However, the more important condition, small value of the residual Coulomb interaction (see section II B), is not always fulfilled for such atoms. This manifests itself in configuration mixing and can be verified by examining the spectra of the open-shell atoms. The states of the $4f^n 6s^2$ configuration are sufficiently pure. Mixing with configurations having different number of $4f$ -electrons is small. This is because the $4f$ electrons are most easily excited into the $5d$ state, but configurations $4f^n 6s^2$ and $4f^{n-1} 5d 6s^2$ do not mix due to different parity. On the other hand, the states of the same parity and total angular momentum but different configurations are high in the spectrum. For example, the first state of erbium which could mix with the $4f^{12} 6s^2$ $^3\text{H}_6$ ground state is the state of the $4f^{11} 6s^2 6p$ configuration with the energy of 19817 cm^{-1} .

In contrast, the states of the $5d^n 6s^2$ configurations are not pure due to mixing with the $5d^{n+1} 6s$ configuration. The same is true for most of the atoms with the $4d^n 5s^2$ or $3d^n 4s^2$ ground state configuration. For example, the $4d^5 5s^2$ $^6\text{S}_{5/2}$ ground state of technetium is mixed with the $4d^6 5s$ $^6\text{D}_{5/2}$ excited state separated by 3701 cm^{-1} only. There are atoms in which such energy interval is large. The approach used in this paper might work for these atoms. This question needs additional study.

III. CONFIGURATION INTERACTION CALCULATION OF POLARIZABILITIES

A. CI+MBPT calculation of polarizabilities

We have demonstrated in previous section that calculation of polarizabilities of atom with open f -shell can be reduced to the calculation of polarizabilities for atoms with two or three valence electrons which form the $6s^2$ or $6s^2 5d$ configurations in lanthanides and $7s^2$ or $7s^2 6d$ configurations in actinides. The open $4f$ or $5f$ shell is

TABLE III: Scalar polarizabilities of lanthanides. All values are given in atomic units.

Z	element	configuration	core	valence (CI+MBPT)	total scalar polarizability (core+valence)	existing data	reference
57	La	$5d6s^2$	7.7	206	213.7	210	calc. [11]
		$5d^26s^1$	7.7	211	218.7	—	—
58	Ce	$4f^15d6s^2$	5.5	199.2	204.7	200	calc. [11]
		$4f^26s^2$	4.1	219.3	223.4	—	—
59	Pr	$4f^36s^2$	4.7	211.1	215.8	190	calc. [11]
		$4f^25d6s^2$	5.3	190.4	195.7	—	—
60	Nd	$4f^46s^2$	5.3	203.1	208.4	212	calc. [11]
		$4f^35d6s^2$	5.1	182.4	187.5	—	—
61	Pm	$4f^56s^2$	5.6	194.6	200.2	203	calc. [11]
		$4f^45d6s^2$	5	174.3	179.3	—	—
62	Sm	$4f^66s^2$	5.8	186.3	192.1	194	calc. [11]
		$4f^55d6s^1$	4.9	166.8	171.7	—	—
63	Eu	$4f^76s^2$	5.9	178.3	184.2	187	calc. [11]
		$4f^65d6s^1$	4.8	159.9	164.7	—	—
64	Gd	$4f^75d6s^2$	4.7	153.6	158.3	159	calc. [11]
		$4f^75d^26s^1$	4.7	189.8	194.5	—	—
65	Tb	$4f^96s^2$	6.1	163.4	169.5	172	calc. [11]
		$4f^85d6s^2$	4.6	147.8	152.4	—	—
66	Dy	$4f^{10}6s^2$	6.1	156.6	162.7	165	calc. [11]
		$4f^95d6s^2$	4.5	142.8	148.3	—	—
67	Ho	$4f^{11}6s^2$	6.2	150.1	156.3	159	calc. [11]
		$4f^{10}5d6s^2$	4.4	138.5	142.9	—	—
68	Er	$4f^{12}6s^2$	6.3	143.9	150.2	153	calc. [11]
		$4f^{11}5d6s^2$	4.4	135	139.4	—	—
69	Tm	$4f^{13}6s^2$	6.3	138	144.3	147	calc. [11]
		$4f^{12}5d6s^2$	4.3	132.5	137.8	—	—
70	Yb	$4f^{14}6s^2$	6.4	132.5	138.9	142	calc. [11]
		$4f^{14}6s^16p^1$	6.4	305.8	312.2	315.9	calc. [37]
71	Lu	$4f^{14}5d6s^2$	4.3	132.9	137.2	148	calc. [11]
		$4f^{14}6s^26p^1$	4.3	57	61.3	—	—

attributed to the core and treated as it is fully occupied but its contribution to the potential is rescaled with the fractional occupation number.

The calculations are performed with the use of the CI+MBPT method. Detailed description of the method can be found in our earlier works [30–32]. A brief description of this method is presented in this section.

We use the V^{N-M} approximation [31]. The core electron states are obtained in Hartree-Fock approximation for $N - M$ electrons, where N and M are total number of electrons and number of electrons above closed shells ("valence electrons"), excluding the f -shell electrons. Contribution of the latter is included in self-consistent potential of the core with "weight", fractional occupation number that is equal to the ratio of $n/14$, where n is number of f -shell electrons. The Hartree-Fock (HF) Hamiltonian of the system has the form

$$\hat{H}_{HF}(r_i) = c\alpha\hat{\mathbf{p}}_i + (\beta - 1)mc^2 - \frac{Ze^2}{r_i} + V^{N-M}(r_i), \quad (14)$$

where $\hat{\mathbf{p}}_i$ and \mathbf{r}_i are operator of momentum and coordinate of electron, V^{N-M} is the self-consistent potential of the core.

Many-electron states for valence electrons can be obtained using the CI and MBPT methods. The effective CI Hamiltonian has the form

$$\hat{H}^{CI} = \sum_{i=1}^M \hat{h}_1(r_i) + \sum_{j>i=1}^M \hat{h}_2(r_i, r_j), \quad (15)$$

where $\hat{h}_1(r)$ is the single-electron operator and $\hat{h}_2(r_i, r_j)$ is the two-electron operator. The single electron operator $\hat{h}_1(r)$ differs from (14) by an extra operator $\Sigma_1(r)$

$$\hat{h}_1(r_i) = \hat{H}_{HF}(r_i) + \Sigma_1(r_i). \quad (16)$$

This Σ_1 operator represents correlation interaction between a particular valence electron and electrons in the

TABLE IV: Scalar polarizabilities of actinides. All values are given in atomic units.

Z	element	configuration	core	valence	total scalar	existing	reference
				(CI+MBPT)	polarizability	data	
					(core+valence)		
89	Ac	$6d7s^2$	10.1	193.3	203.3	217	calc. [11]
		$7s^27p^1$	10.1	131.8	141.9	—	—
91	Pa	$5f^26d7s^2$	3.8	150.6	154.4	171	calc. [11]
		$5f^26d^27s^1$	3.8	148.1	151.9	—	—
92	U	$5f^37s^26d$	3.8	124.0	127.8	137(10)	exp. [40]
		$5f^47s^2$	4.3	148.9	153.2	152.7	calc. [11]
93	Np	$5f^46d7s^2$	4.8	145.7	150.5	167	calc. [11]
		$5f^57s^2$	5.8	121.7	127.5	—	—
94	Pu	$5f^67s^2$	6.5	125.7	132.2	165	calc. [11]
		$5f^56d7s^2$	5.2	142.4	147.6	—	—
95	Am	$5f^77s^2$	7.2	124	131.2	157	calc. [11]
		$5f^66d7s^2$	5.4	139.3	144.7	116	calc. [41]
96	Cm	$5f^76d7s^2$	5.6	137	143.6	155	calc. [11]
		$5f^87s^2$	7.6	121	128.6	—	—
97	Bk	$5f^97s^2$	8	117.3	125.3	153	calc. [11]
		$5f^86d7s^2$	5.8	135.8	141.6	—	—
98	Cf	$5f^{10}7s^2$	8.2	113.3	121.5	138	calc. [11]
		$5f^96d7s^2$	5.8	136.5	142.3	—	—
99	Es	$5f^{11}7s^2$	8.3	109.2	117.5	133	calc. [11]
		$5f^{10}6d7s^2$	5.9	140.2	146.1	—	—
100	Fm	$5f^{12}7s^2$	8.4	105	113.4	161	calc. [11]
		$5f^{11}6d7s^2$	6	149.6	155.6	—	—
101	Md	$5f^{13}7s^2$	8.5	100.9	109.4	123	calc. [11]
		$5f^{12}6d7s^2$	6	173.6	179.6	—	—
102	No	$5f^{14}7s^2$	8.5	96.9	105.4	118	calc. [11]
		$5f^{14}7s^17p^1$	8.5	259.3	267.8	110.8	calc. [36]
						—	—

core. The two electron part of (15) is given by

$$\hat{h}_2(r_i, r_j) = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \Sigma_2(r_i, r_j), \quad (17)$$

where Σ_2 accounts for screening of Coulomb interaction between valence electrons by core electrons. For our purposes Σ_1 and Σ_2 operators are sufficient to be accounted in the lowest, second order of the MBPT.

The CI many-electron wave function is written in a form

$$\Psi = \sum_k c_k \Phi_k(r_1, \dots, r_M), \quad (18)$$

where Φ_k are determinants made of single electron eigenfunctions of (14) combined in a way to have appropriate value of total angular momentum J . Here total angular momentum J is not the actual total angular momentum of the $4f^{M-2}6s^2$ or $4f^{M-3}6s^25d$ configuration, but the total angular momentum of smaller subsystem, e.g. $J = 0$ for the $6s^2$ configuration of valence electrons and $J = 3/2$

or $5/2$ for the $6s^25d$ configuration. The expansion coefficients c_k and corresponding energies are found by solving the matrix eigenvalue problem

$$\hat{H}^{CI}\Psi = E\Psi \quad (19)$$

for lowest states of definite J and parity.

Electric dipole transition amplitudes in (3) are calculated using the time-dependent Hartree-Fock method [33] (which is equivalent to the RPA method) and the CI method

$$\langle a|D_z|n \rangle = \left\langle \Psi^{(a)} | d_z + \delta V^{N-M} | \Psi^{(n)} \right\rangle, \quad (20)$$

where $d_z = -ez$ is the z -component of the dipole moment operator and δV^{N-M} is the correction to core potential due to its polarization by external electric field. Electron wavefunctions $\Psi^{(a)}$ and $\Psi^{(n)}$ were obtained using described above technique.

To calculate scalar polarizabilities using formula (3) summation over complete set of intermediate many-electron states needs to be carried out. We use the

Dalgarno-Lewis method [34] to reduce this summation to solving a system of linear equations with the CI matrix. The expression for the polarizability (3) is rewritten as

$$\alpha_0(a) = \frac{2}{3(2J_2 + 1)} \sum_{J_3=J_2\pm 1} \langle \delta\Psi_{J_3}^{(a)} || \mathbf{d} || \Psi_{J_2}^{(a)} \rangle, \quad (21)$$

where J_2 is total angular momentum of valence electrons. The correction $\delta\Psi_{J_3}^{(a)}$ to the wavefunction $\Psi_{J_2}^{(a)}$ due to the laser electric field is found from the matrix equation

$$(H^{CI} - E_a) \delta\Psi_{J_3}^{(a)} = -(d_z + \delta V^{N-M}) \Psi_{J_2}^{(a)}. \quad (22)$$

B. CI calculations for systems with many valence electron.

Previous consideration was based on the assumption that f -electrons can be attributed to the core and the problem can be reduced to two or three valence electrons above closed shells. This allows us to use very advanced and accurate CI+MBPT method to perform the calculations. It is useful however to check the calculations with an alternative technique which is free from the assumption, even though the technique is less accurate. In this section we move f -electrons back to the valence space and use the CI technique which treat them the same way as other valence electrons. The total number of valence electrons for atoms with open f -shell varies between four and sixteen. Below we consider examples of dysprosium, erbium and thulium atoms in the $4f^{10}6s^2$, $4f^{12}6s^2$ and $4f^{12}6s^2 5d$ configuration respectively. The number of valence electrons is twelve for Dy, fourteen for Er and fifteen for Tm. The use of the CI+MBPT method considered above is not possible for so large number of valence electrons. We use an alternative CI technique developed in our earlier works [43, 44]. This technique does not use excited single-electron states in the basis. It tries instead to optimize the basis made of the lowest single-electron states. The Hartree-Fock Hamiltonian used to construct the basis has the form

$$\hat{H}_B = \sum_{i=1}^N c\alpha \hat{\mathbf{p}}_i + (\beta - 1)mc^2 - \frac{Ze^2}{r_i} + V^N(r_i) \quad (23)$$

Here V^N is the self-consistent Hartree-Fock potential created by all atomic electrons. It is considered to be different for different configurations of valence electrons (see Ref. [43, 44] for details). The CI Hamiltonian has the form

$$\hat{H}_{CI} = \sum_{i=1}^M \left[c\alpha \hat{\mathbf{p}}_i + (\beta - 1)mc^2 - \frac{Ze^2}{r_i} + V^{N-M}(r_i) + \delta V(r_i) \right] + \sum_{j>i=1}^M \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (24)$$

where M is the number of electrons above closed shells. Apart from the number of valence electrons the CI Hamiltonian (24) has two important differences from the CI+MBPT Hamiltonian (15), the Σ_2 operator is not included and the Σ_1 operator is approximated by a parametric potential in a form

$$\delta V(r_i) = -\frac{\alpha_p}{2(r_i^4 + a^4)}. \quad (25)$$

Here a is roughly core radius (we use $a = a_B$). The form of (25) is chosen to match the long range polarization potential. Therefore, α_p is effectively core polarizability. It is assumed to be different for different configurations. This allows us to fit energy intervals between states of different configurations by treating α_p as a fitting parameter.

Using this method to construct the wave function of the ground state and hundreds of states for the summation in (3) and using the RPA method to calculate amplitudes (20) we calculate polarizabilities of many-electron atoms. This method was used for the $4f^{10}6s^2$ configuration of Dy [20] and the $4f^{12}6s^2$ configuration of Er [17]. In this work we reevaluated polarizabilities of Dy and Er using extended basis and calculated the polarizability of the first state of the $4f^{12}6s^2 5d$ configuration of Tm ($E = 13119.61 \text{ cm}^{-1}$). The results, $\alpha_0 = 165 \text{ a.u.}$ for Dy, $\alpha_0 = 169 \text{ a.u.}$ for Er, and $\alpha_0 = 122 \text{ a.u.}$ for Tm are in good agreement with the results reported in previous section.

IV. RESULTS

The results for scalar polarizabilities of ground and first excited configurations of lanthanides and actinides are presented in tables III and IV. Total scalar polarizability is a sum of core electron (forth column) and valence electron (fifth column) contributions. Core electron contribution is calculated using the RPA approximation described in section II A. Valence f -shell electrons contribution was accounted in the core as closed f -shell with fractional occupation number equal to $n/14$, where n is the number of f -shell electrons. Contribution of remaining valence electrons presented in fifth column in tables III and IV were obtained using the CI+MBPT method described in section III. All presented values are in atomic units. In approximation used in this paper scalar polarizabilities do not depend on the values of total angular momentum as it was shown in section II C, therefore their values are the same for all levels of a given configuration. Two last columns represent results from [11] and some other sources for comparison. As one can notice, agreement is quite good although employed methods are quite different. Extended estimate of accuracy together with comparison with available experimental measurements is presented in next section.

V. DISCUSSION OF ACCURACY

To estimate accuracy of present calculations we compare the results obtained in different approaches used in this and earlier works. We also compare the results with available experimental data. There are strong indications that the accuracy of present calculations is on the level of 15% or better.

Test calculations with the use of the many-valence-electrons CI method described in section IIIB show no more than 13% deviation from the results presented in Table III. Given that that method is likely to be less accurate than the main CI+MBPT method used in present work, the actual accuracy of the results presented in Tables III and IV might be better.

We use expression (11) to calculate scalar polarizabilities. Note that this expression does not depend on the total angular momentum of the atom, J_a . It does not also depend on the total angular momentum of the f -subshell, J_1 . However, it does depend on the total angular momentum of remaining valence electrons, J_2 , which is strictly speaking is not known. This does not lead to a problem for the $4f^n 6s^2$ configurations since $J_2 = 0$ for the $6s^2$ configuration. If we consider the $4f^{n-1} 6s^2 5d$ configuration instead, which is divided into the $4f^{n-1}$ and $6s^2 5d$ subsystems, then there are two possibilities for the $6s^2 5d$ subsystem, $J_2 = 3/2$ and $J_2 = 5/2$. It is important to check that the results are the same for both cases. We have done this test for gadolinium atom. Calculations for the $4f^7 6s^2 5d$ configuration assuming $J_2 = 3/2$ led to $\alpha_0 = 153.6$ a.u. (see Table III) while calculations with $J_2 = 5/2$ gave $\alpha_0 = 153.8$ a.u., the difference is about 0.1%.

The most complete other theoretical data comes from the calculations of Doolen [11]. Estimated accuracy of these calculations is 25%. However, as one can see from Tables III and IV the agreement between two sets of results is significantly better for most of atoms. It is about 10% for lanthanides and slightly worse for actinides. There is a special case of fermium atoms where the result of Ref. [11] jumps to a high value breaking the trend along the row of actinides. In contrast, the change in the value of scalar polarizabilities for actinides is very smooth in our calculations. We see no reason for fermium to be very different from its neighbors. The difference between our results and those of Ref. [11] for other actinides varies between 7 and 20%, being smaller than 15% for most of atoms.

The most detailed study of the polarizabilities of lanthanides has been done for ytterbium atom. This is because it has relatively simple electron structure with fully filled $4f$ subshell and because it has the $^1S_0 - ^3P_0^\circ$ transition which is suitable for atomic clocks. The available theoretical and experimental data for these two states of ytterbium is summarized in Table V. Our result for the ground state of Yb is within 5% of other accurate calculations and experimental limits found in Ref. [39]. The result for the excited $6s6p\ ^3P_0^\circ$ state is less accurate but still within 12% of other accurate calculations and experimental limits.

Experimental data on static scalar polarizabilities of lanthanides and actinides is absent. There are measurements of the dynamic polarizabilities for dysprosium [24], erbium [25], and uranium [40]. Scalar polarizability of uranium interpolated to $\omega = 0$ is 137(10) a.u. [40] which differ by about 10% from our calculated value of 153 a.u. (see Table V). The situation for dysprosium and erbium is different. Measured dynamic polarizabilities of both atoms are significantly smaller than the calculated static polarizabilities. For example, $\alpha_0(\lambda = 1064\text{ nm}) = 116$ a.u. for Dy [24], and $\alpha_0(\lambda = 1064\text{ nm}) = 84(2)(18)$ a.u. for Er [25], while calculated static polarizabilities are 163 a.u. for Dy and 150 a.u. for Er (see Table III). If all numbers are correct than the most likely explanation for the shift in the polarizabilities is the presence of a strong resonance between $\omega = 0$ and $\omega = 8398\text{ cm}^{-1}$ ($\lambda = 1064\text{ nm}$). There is indeed resonances in both atoms which correspond to the $4f - 5d$ single-electron transitions. However, according to our estimations, the amplitudes of the transitions between ground and resonance states are too small to explain the difference between theory and experiment. Another possible explanation relies on tensor polarizability. If tensor polarizability is large, then depending on the geometry of the measurements, the effective polarizability might be small. However, here again our estimations show that tensor polarizabilities of both atoms are too small to explain the difference. In the end the reason for disagreement is not clear. However, based on the arguments presented above, we believe that the accuracy of our result is about 15% or better.

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TABLE V: Calculated and experimental static scalar polarizabilities of ytterbium (in a.u.).

Z	element	State	core	valence	total scalar polarizability (core+valence)	existing data	reference
70	Yb	$4f^{14}6s^2\ ^1S_0$	6.4	132.5	138.9	142 144.6 140.7 141(6) 142.6 $134.4(1.0) \leq \alpha_0 \leq 144.2(1.0)$	calc. [11] calc. [35] calc. [36] calc. [37] calc. [38] exp. [39]
		$4f^{14}6s6p\ ^3P_0^o$	6.4	305.8	312.2	315.9 252(25) 266(15) 302(14) $280.1(1.0) \leq \alpha_0 \leq 289.9(1.0)$	calc. [37] calc. [42] calc. [7] calc. [37] exp. [39]

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